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1,2,2,6,6-PENTAMETHYL-4-(ω-BROMOALKOXY)PIPERIDINES AND A METHOD FOR THEIR PREPARATION

[1,2,2,6,6-Pentametyl-4-(ω-bróm-alkoxy)piperidíny a spôsob ich prípravy]

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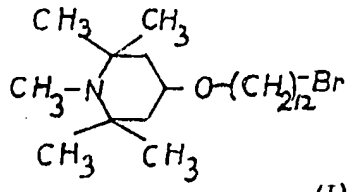
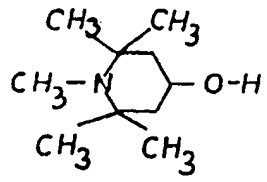
This development pertains to the 1,2,2,6,6-pentamethyl-4-(ω-bromoalkoxy)piperidines of Formula I and a method for their preparation that consists of leaving the 1,2,2,6,6-pentamethl-4-hydroxy-piperidine of Formula II to react with the α,ω-dibromalkane of Formula III during intensive mixing in a heterophase system where the aqueous solution of alkaline hydroxide forms one phase and the organic solvent that was not miscible with the aqueous phase forms the second phase in the presence of a catalyst of the onium salt type within a temperature interval of 10 to 100°C. The compounds of Formula I are useful as light stabilizers for polymers.



(I)

where

n is 2 to 12



(II)

(III)

where

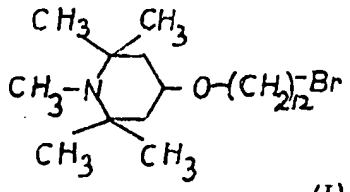
n is 2 to 12.

This invention pertains to the 1,2,2,6,6-pentamethyl-4-(ω-bromo-alkoxy)piperidines and a method for their production.

Sterically shielded amines are currently among the most effective light stabilizers for polymers [F.E. Karrer, *Makromol. Chem.* [*Macromolecular Chemistry*], **181**, 595 (1980), F. Gugumus, *Developments in Polymer Stabilisation-1*, Edited by G. Scott, *Applied Sciences Publishers*, London [sic], 1979, Chapter 8; J.J. Usilton, A.R. Patel, *Am. Chem. Soc.*, "Polymer Preparation", **18** (1), 393 (1977)].

There are various derivatives of 2,2,6,6-tetramethylpiperidine, 1,2,2,6,6-pentaalkylpiperidine, 2,2,6,6-tetraalkylpiperazine or 7,15-diazadispiro[5,1,5,3]hexadecane. These compounds inhibit the undesirable degradation processes that occur when light and oxygen interact with polymers. The shortcoming of this group of light stabilizers is their high volatility and the extractability of low-molecular derivatives from polymers. The compounds that are the subject of this invention contain functional ω-bromoalkoxy groups in their molecules. The presence of these groups in a molecule of the light stabilizer increases its molecular weight and also enables further modification of the basic skeleton. These compounds have not been described as yet in the specialized literature.

The 1,2,2,6,6-pentamethyl-4-(ω-bromoalkoxy)piperidines of Formula I



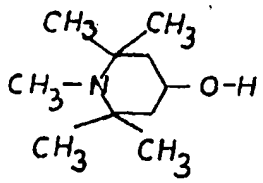
(I)

where

n is 2 to 12

are the subject of the invention.

A method for producing the compounds of Formula I, which is distinguished by the fact that the 1,2,2,6,6-pentamethyl-4-hydroxy-piperidines of Formula II



(II)

react with α,ω-dibromoalkane of Formula III

$$Br-(CH_2)_n-Br \qquad (III)$$

where

n is 2 to 12 in a heterophase system where an aqueous solution of alkaline hydroxide, preferably potassium hydroxide in a concentration range of 5 to 70 percent or sodium hydroxide in a concentration range of 5 to 50% forms one phase while an organic solvent such as benzene, toluene or xylenes that are not miscible with the aqueous phase form the second phase in the presence of a catalyst of the onium salt type such as tetrabutylammonium chloride, tetrabutyl-ammonium bromide, tetrabutylammonium hydrogen sulfate or tetrabutyl-phosphonium bromide used in a quantity of 1 to 10 mol.%

per quantity of Compound II in a temperature interval of 10 to 100°C is also the subject of the invention.

Example 1

1,2,2,6,6-Pentamethyl-4-hydroxypiperidine in the amount of 8.56 grams (0.05 moles), 1.61 grams (0.005 moles) of tetrabutylammonium bromide, 9.4 grams (0.05 moles) of 1,2-dibromomethhane, 10 ml of benzene and 15 ml of a 50% solution of sodium hydroxide were mixed intensively at room temperature for 30 hours. At this point, an organic layer separated out which was rinsed with water and brine and dried with anhydrous sodium sulfate. The solvent was distilled out and the product was distilled under vacuum. A fraction of colorless liquid was collected in the temperature interval of 120 to 130°C at a pressure of 333 Pa.

Elemental analysis for $C_{12}H_{24}BrNO$:

Calculated:

51.80% C; 8.69% H; 5.03% N,

Actually found:

51.38% C; 8.46% H; 4.89% N.

^1H NMR spectrum ($CDCl_3$):

δ (ppm) =

0.97 (s, $-CH_3$ ax, 6H),

1.12 (s, $-CH_3$ eq, 6H),

1.23 to 1.93 (m, $-CH_2-$, 4H),

2.17 (s, $N-CH_3$, 3H),

3.37 (t,-CH_2-Br, 2H, J=6 Hz),

3.40 (t,-CH_2- 2H, J=6 Hz),

3.40 to 4.00 (m, =CH-O-, 1H).

Example 2

1,2,2,6,6-Pentamethyl-4-hydroxypiperidine in the amount of 8.56 grams (0.05 moles), 0.34 grams (0[.]001 moles of tetrabutylammonium hydrogen sulfate, 10.80 grams (0.05 moles) 1,4-dibromobutane, 10 ml of toluene and 15 ml of 30% potassium hydroxide were mixed intensively at 50°C for 20 hours.

The reaction mixture was then processed exactly as in Example 1. A fraction of colorless liquid was collected during distillation in the temperature range of 130 to 140°C at a pressure of 333 Pa.

Elemental analysis for $C_{14}H_{28}BrNO$:

Calculated:

54.90% C; 9.21% H; 4.57% N;

Actually found:

54.48% C; 9.25% H; 4.49% N.

^{1}H NMR spectrum ($CDCl_3$):

δ(ppm) =

0.97 (s,-CH_3 ax, 6H),

1.12 (S,-CH_3 eq, 6H),

1.23 to 2.00 (m,-CH_2-, 8H),

2.17 (s, CH_3-N,3H),

3.37 (t,-CH_2-O-, 2H),

3.40 (t,-CH_2-B4, 2H),

3.40 to 4.00 (m,=CH-O-, 1H).

Example 3

1,2,2,6,6-Pentamethyl-4-hydroxypiperidine in the amount of 8.56 grams (0.05 moles) 0.68 grams (0.002 moles) of tetrabutylphosphonium bromide, 12.2 grams (0.05 moles) of 1,6-dibromohexame, 10 ml of a mixture of xylenes with a distillation range of 137 to 140°C were mixed intensively at 100°C for 8 hours.

The reaction mixture was then processed exactly as in Example 1. A fraction of colorless liquid was collected during distillation in a temperature range of 180 to 190°C at a pressure of 333 Pa.

Elemental analysis for $C_{16}H_{32}BrNO$:

Calculated:

57.47% C; 9.65% H; 4.19% N;

Actually found:

57.69% C; 10.05% H; 4.11% N.

^1H NMR spectrum ($CDCl_3$);

δ (ppm) =

0.97 (s, -CH_3 ax, 6H),

1.11 (s, -CH_3 eq, 6H),

1.17 to 1.93 (m, -CH_2-, 12H),

2.15 (s, CH_3-N, 3H),

3.35 (t, -CH_2-O-, 2H, J=6 Hz),

3.39 (t, -CH_2-Br, 2H, J=6 Hz),

3.40 to 4.00 (m, =CH-O-, 1H).

Example 4

1,2,2,6,6-Pentamethyl-4-hydroxypiperidine in the amount of 8.56 grams (0.05 moles), 1.61 grams (0.005 moles) of tetrabutylammonium bromide, 13.6 grams (0.05 moles) of 1,8-dibromoctane, 10 ml of benzene and 15 milliliters of 15% potassium hydroxide were mixed intensively at 50°C for 20 hours.

The reaction mixture was then processed exactly as in Example 1. A fraction of colorless liquid was collected during distillation in the temperature interval of 185 to 195°C at a pressure of 300 Pa.

Elemental analysis for $C_{18}H_{36}BrNO$:

Calculated:

59.65% C; 10.01% H; 3.87% N;

Actually found:

60.16% C; 10.16% H; 3.70% N.

^1H NMR spectrum ($CDCl_3$):

δ (ppm) =

0.97 (s, $-CH_3$ ax, 6H),

1.12 (s, $-CH_3$ eq, 6H),

1.20 to 2.00 (m, $-CH_2-$, 16H)

2.17 (s, CH_3-N, 3H),

3.35 (t, $-CH_2-O-$, 2H, J=6 Hz),

3.39 (t, $-CH_2-Br$, 2H, J=6 Hz),

3.40 to 4.00 (m, =CH-O-, 1H).

Example 5

1,2,2,6,6-Pentamethyl-4-hydroxypiperidine in the amount of 8.56 grams (0.05 moles), 1.61 grams (0.005 moles) of tetrabutylammonium bromide, 15.0 grams (0.005) moles of 1,10-dibromodecane, 10 ml of benzene and 15 milliliters of a 50% solution of sodium hydroxide were mixed intensively at room temperature for 30 hours.

The reaction mixture was then processed exactly as in Example 1. A fraction of colorless liquid was collected during distillation in the temperature interval of 190 to 200°C at a pressure of 200 Pa.

Elemental analysis for $C_{20}H_{40}BrNO$:

Calculated:

61.52% C; 10.33% H; 3.59% N;

Actually found:

62.48% C; 10.90% H; 3.77% N.

^1H NMR spectrum ($CDCl_3$):

δ(ppm) =

0.97 (s, $-CH_3$ ax, 6H),

1.12 (s, $-CH_3$ eq, 6H),

1.17 to 2.00 (m, $-CH_2-$, 20H),

2.17 (s, CH_3-N, 3H),

3.27 (s, $-CH_2-O-$, 2H, J=6 Hz),

3.30 (t, $-CH_2-Br$, 2H, J=6.5 Hz),

3.30 to 4.00 (m, =CH-O-, 1H).

Example 6

1,2,2,6,6-Pentamethyl-4-hydroxypiperidine in the amount of 8.56 grams (0.05 moles), 1.61 grams (0.005 moles) of tetrabutylammonium bromide, 16.41 g (0.05 moles) of 1,12-dibromododeccane, 10 ml of benzene and 15 ml of 50% sodium hydroxide were mixed intensively at room temperature for 30 hours. The reaction mixture was then processed exactly as in Example 1. A fraction of colorless liquid was collected during distillation in the temperature interval of 195 to 205°C at a pressure of 173 Pa.

Elemental analysis for $C_{22}H_{44}BrNO$:

Calculated:

63.14% C; 10.60% H; 3.35% N;

Actually found:

62.10% C; 10.21% H; 3.41% N.

^1H NMR spectrum ($CDCl_3$):

δ (ppm) =

0.97 (s,-CH_3 ax, 6H),

1.12 (s,-CH_3 eq, 6H),

1.17 to 1.95 (m,-CH_2-, 24H),

2.17 (s, CH_3-N, 3H),

3.27 (t,-CH_2-O-, 2H, J = 6 Hz),

3.31 (t,-CH_2-Br, 2H, J = 6.5 Hz),

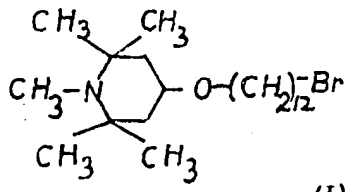
3.31 to 4.01 (m, =CH-O-, 1H.

Example 7

100 parts by weight of unstabilized powdered polypro-pylene were impregnated in dichloromethane with 0.1 parts by weight 2,6-di-tert.butyl-4-methylphenol, 0.15 parts by weight calcium stearate and 0.2 parts by weight of a compound prepared in accordance with Example 6. After the solvent had been evaporated from the mixture, film with a thickness of 0.2 mm was pressed out at a pressure of 20 MPa and temperature of 190°C over a period of 3 minutes. The film produced in this manner was subjected to mercury lamp illumination at a level of 125 Watts and a distance of 7 cm from the source. Degradation of the polymer was monitored by the development of a carbonyl band in the infrared spectra. Where the time for achieving a carbonyl index of 0.2 for pure polypropylene is 240 hours, the stabilized polymer reached this value only after 1,560 hours.

CLAIMS OF THE INVENTION

1. 1,2,2,6,6-Pentamethyl-4-(ω-bromoalkoxy)-piperidine with Formula I



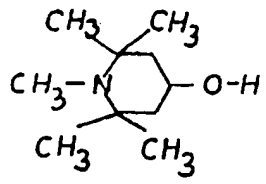
(I)

where

N is 2 to 12

is the subject of the invention.

2. The method used to prepare the 1,2,2,6,6-pentamethyl-4-(ω-bromoalkoxy)piperidines of Formula 1 in accordance with paragraph 1 is distinguished by the fact that the 1,2,2,6,6-pentamethyl-4-hydroxypiperidine with Formula II



(II)

is left to react with α,ω-dibromoalkane with Formula III

$$Br-(CH_2)_n-Br \qquad (III)$$

where

n is 2 to 12 in a heterophase system with intensive mixing where an aqueous solution of alkaline hydroxide forms one phase and an organic solvent that is not miscible with the aqueous phase forms the second phase in the presence of a catalyst of the onium salt type in a temperature interval of 10 to 100°C.

3. The method based on point 2 is distinguished by the fact that sodium hydroxide in a concentration range of 5 to 50% or potassium hydroxide in a concentration range of 5 to 70% is used as the alkaline hydroxide.

4. The method based on point 2 is distinguished by the fact that benzene, toluene or a mixture of xylenes is used as the organic solvent that is not miscible with the aqueous phase.

5. The method based on point 2 is distinguished by the fact that onium salts such as tetrabutylammonium chloride, tetrabutylammonium hydrogen sulfate or tetrabutylphosphonium bromide are used as the reaction catalyst in the amount of a 1 to 10 mol.% ratio to the original amount of 1,2,2,6,6-pentamethyl-4-hydroxypiperidine.